Journal of Chromatography, 114 (1975) 29–38

CHROM. 8428

PHYSICO-CHEMICAL AND GAS–SOLID CHROMATOGRAPHIC EVALUATION OF SURFACE-MODIFIED SILICA GELS

A. G. DATAR and P. S. RAMANATHAN

Analytical Chemistry Division, Bhabha Atomic Research Centre, Modular Laboratories, Trombay, Bombay-400 085 (India)

(Received April 8th, 1975)

SUMMARY

Silica gel samples coated with copper(II) tetra-ammonium sulphate, copper(II) bisethylenediamine sulphate and copper(II) bistriethanolamine sulphate were investigated by differential thermal analysis and thermogravimetric analysis. Surface area measurements were made in order to determine the influence of loading on the surface area. Gas–solid chromatographic studies were then carried out in order to evaluate silica gel and surface-modified silica gels as potential adsorbents in gas chromatography. Graphs of retention time against percentage loading of copper were plotted at different temperatures for a large number of gases and vapours. Some possible gas chromatographic separations that can be achieved with the use of surface-modified silica gels as stationary phase are also indicated.

INTRODUCTION

During the last few years, the results of several investigations on the utility of surface-modified solids as adsorbents in gas chromatography (GC) have been published[1,2]. While extensive work has been carried out on salt-modified silica gels[3–6], the number of investigations on silica gel (SG) loaded with complex compounds appears to be small[7,8].

This paper summarises the results of physico-chemical and GC investigations of SG loaded with three complex copper(II) compounds, *viz.*, copper(II) tetraammonium sulphate, copper(II) bisethylenediamine sulphate and copper(II) bistriethanolamine sulphate.

EXPERIMENTAL AND RESULTS

Loading studies

Loading studies were carried out by the batch equilibration procedure, using chromatography-grade SG (60–120 mesh; B.D.H., Poole, Great Britain). Some typical curves depicting the variation of the function K (moles of Cu^{2+} taken up per gram of SG/moles of Cu^{2+} left per millilitre of solution) with concentration and time are given in Fig. 1.

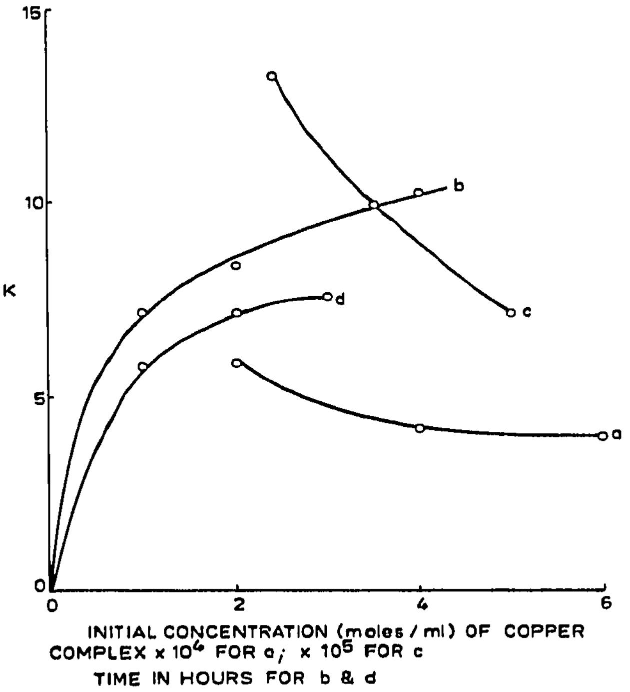

Fig. 1. Variation of K with concentration and time. Curves a and b, copper tetraammonium sulphate; c and d, copper bisethylenediamine sulphate. Time of equilibration: a, 1 h; c, 2 h. Initial concentration of copper tetraammonium sulphate, $1.0 \cdot 10^{-4}$ moles/ml for curve b; initial concentration of copper bisethylenediamine sulphate, $5.0 \cdot 10^{-5}$ moles/ml for curve d.

Thermal studies

An apparatus constructed in this Division[9] was employed for the differential thermal analysis (DTA) of SG and surface-modified silica gel (SMSG) samples. Thermogravimetric analyses (TGA) were carried out on a Cahn RG electrobalance. Typical DTA curves are shown in Fig. 2 and TGA curves in Fig. 3.

Surface area measurements

The surface areas (SA) of the adsorbents (SG and SMSG) were determined (after drying the samples at 110° by the continuous flow method[10] using a home-made apparatus[11]. The variation of SA with percentage loading is shown in Fig. 4.

Gas chromatographic studies

A home-made gas chromatograph with a thermal conductivity detector[12] was used for all of the studies.

A copper column, 1.5 ft. × 1/8 in., was used with hydrogen as carrier gas at the flow-rate of 50 ml/min. The column temperatures at which GC studies were carried out were −78°, 0°, 30°, 60° and 120°. The columns of SG and SMSG were heated at 110° for about 2 h and then cooled in a stream of dry nitrogen before carrying out the GC experiments.

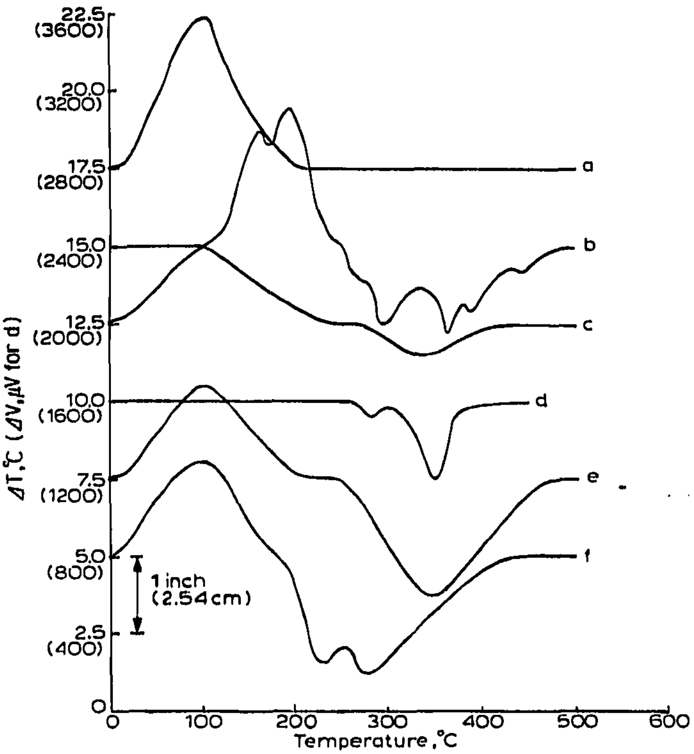

Fig. 2. DTA curves for complexes, silica gel and surface-modified silica gels. Linear heating rate: 10°/min; static air atmosphere. a, SG (100.0 mg); b, copper tetraammonium sulphate (103.2 mg); c, SG modified with copper tetraammonium sulphate (103.9 mg); d, copper bisethylenediamine sulphate (see ref. 14); e, SG modified with copper bisethylenediamine sulphate (99.8 mg); f, SG modified with copper bistriethanolamine sulphate (100.2 mg).

The retention characteristics of some inorganic gases (He, O_2, N_2, Ar, CO, CO_2 and N_2O) and organic compounds (*n*-alkanes, unsaturated aliphatic hydrocarbons, chloromethanes, alcohols, ketones, ethers and aromatic compounds) were studied on all of the supports at all of the above temperatures. Some typical curves of retention time (t_R) against percentage loading (PL) of copper are given in Figs. 5 and 6.

DISCUSSION

Curves b and d in the plots in Fig. 1 of K *versus* contact time do not flatten out satisfactorily even when the contact time is 3 h. The situation is the same even when stronger solutions of the complexes (0.4–0.6 M) are employed for equilibration. When the time of contact is fixed, K continuously decreases with increase in the concentration of the solution used for equilibration (curves a and c in Fig. 1).

The results of thermal studies are summarised in Table I.

From the thermal studies, it was concluded that all three complexes show

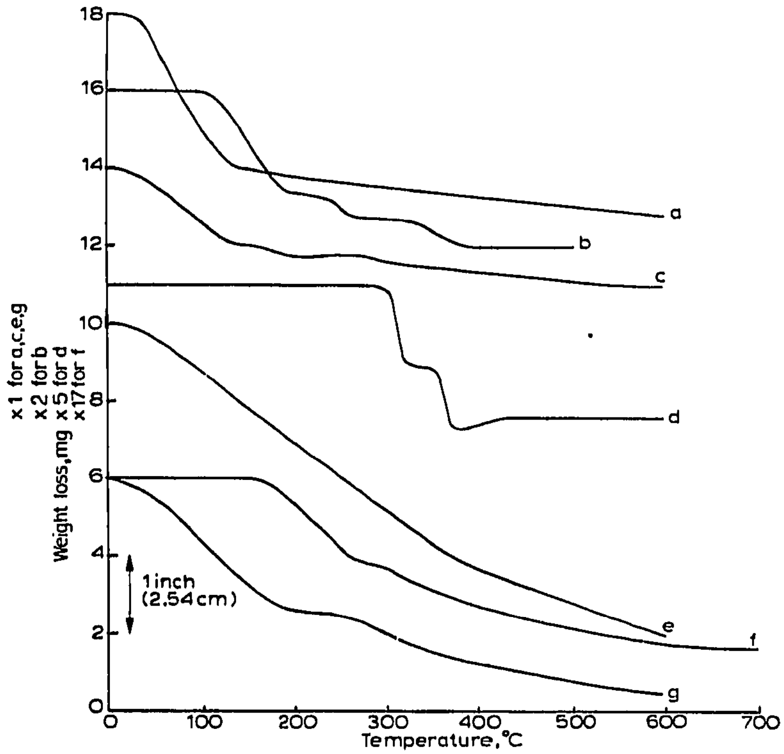

Fig. 3. TG curves for complexes, silica gel and surface-modified silica gels. Linear heating rate: 6°/min; static air atmosphere. a, SG (50.1 mg); b, copper tetraammonium sulphate (21.6 mg); c, SG modified with copper tetraammonium sulphate (12.5% copper; 20.4 mg); d, copper bisethylenediamine sulphate (see ref. 14) (50–55 mg); e, SG modified with copper bisethylenediamine sulphate (4% copper; 45.1 mg); f, copper bistriethanolamine sulphate (see ref. 15) (100.0 mg); g, SG loaded with copper bistriethanolamine sulphate (3.3% copper; 51.5 mg).

enhanced thermal stability when loaded on an SG matrix (owing to solid–solid interactions).

The surface areas show, in general, an initial rapid decrease with increase in percentage loading. The rate of decrease drops considerably at about a 2.5% loading of copper in all instances.

In GC studies, the SG samples with the highest loading contained 10%, 3.8% and 4.0% of copper, respectively, in the three cases investigated. An idea of the separations that can be achieved on SG and SMSG at different temperatures is given in Table II.

With *n*-alkanes, an increase in PL reduces the t_R and tailing. At any chosen temperature, it is therefore possible to elute from SMSG columns the first few higher members of the homologous series that are not eluted from a pure SG column under identical operating conditions. The variation of t_R with PL follows, in general, the pattern of surface area variations. For the same *n*-alkane, sharper peaks with less tailing can be obtained on CELSG columns compared with the other two (with the same percentage loading of copper). For example, at 120°, *n*-octane is eluted after

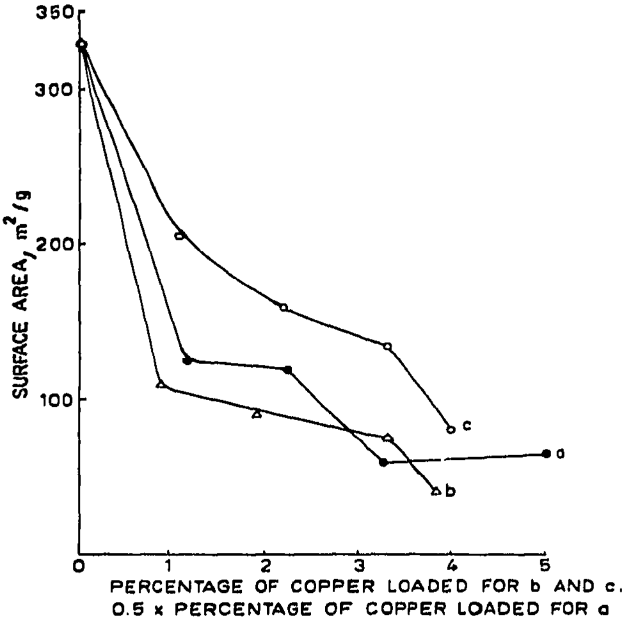

Fig. 4. Variation of surface area with percentage loading. a, SG loaded with copper tetraammonium sulphate; b, SG loaded with copper bisethylenediamine sulphate; c, SG loaded with copper bistriethanolamine sulphate.

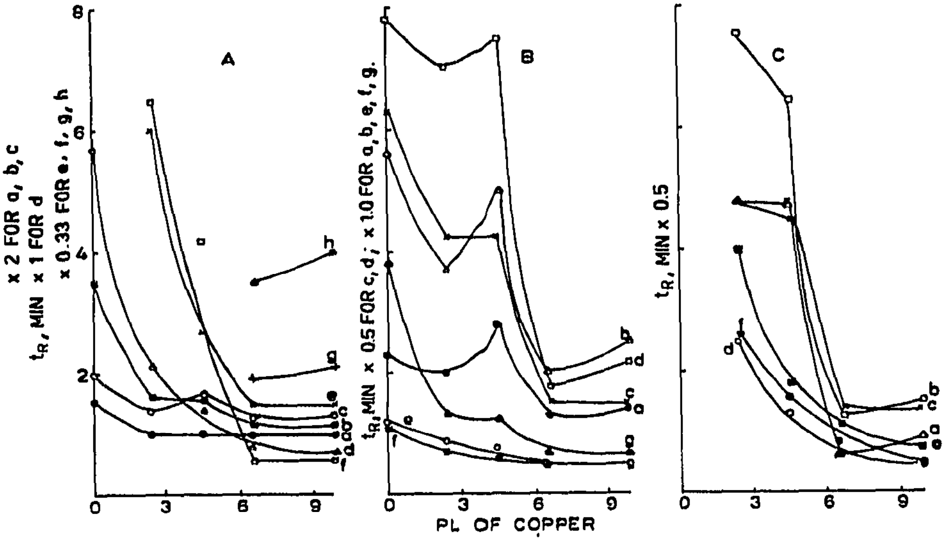

Fig. 5. Variation of t_R with PL of copper (loaded as CA complex). A: a, O_2–N_2 at −78°; b, CH_4 at −78°; c, CO at −78°; d, C_3H_8 at 0°; e, *n*-octane at 120°; f, benzene at 120°; g, toluene at 120°; h, xylene at 120°. B: a, CO_2–N_2O at 0°; b, C_2H_2 at 0°; c, butene-1 at 30°; d, butadiene-1,3 at 30°; e, C_2H_2 at 120°; f, CO_2–N_2O at 120°; g, butene-1 at 120°. C: a, CH_2Cl_2 at 60°; b, $CHCl_3$ at 60°; c, CCl_4 at 60°; d, CH_2Cl_2 at 120°; e, $CHCl_3$ at 120°; f, CCl_4 at 120°.

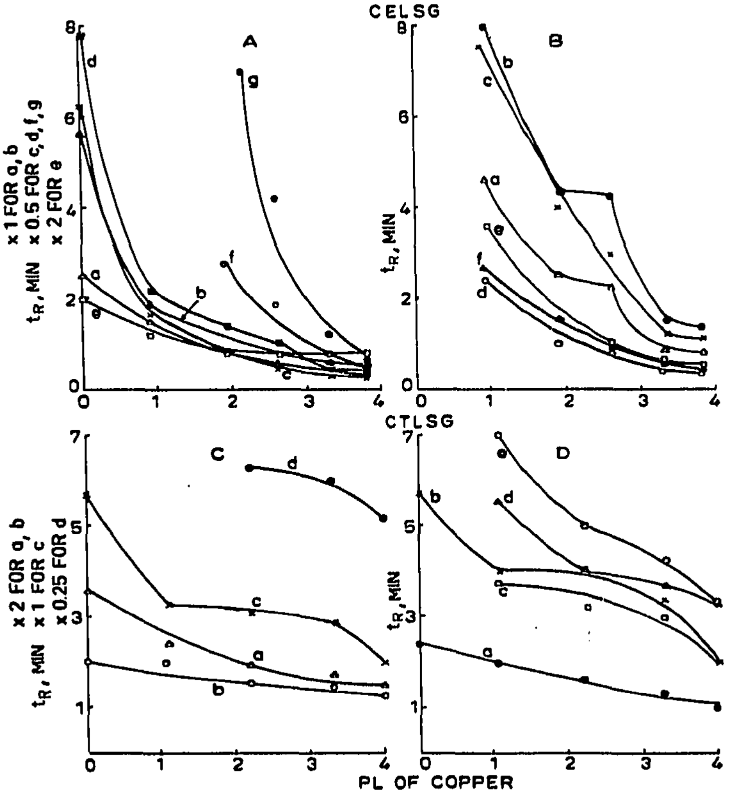

Fig. 6. Variation of t_R with PL of copper. A and B, CELSG; C and D, CTLSG. A: a, CO_2–N_2O at 0°; b, C_2H_2 at 0°; c, butene-1 at 30°; d, butadiene-1,3 at 30°; e, CO at −78°; f, toluene at 120°; g, xylene at 120°. B: a, CH_2Cl_2 at 60°; b, $CHCl_3$ at 60°; c, CCl_4 at 60°; d, CH_2Cl_2 at 120°; e, $CHCl_3$ at 120°; f, CCl_4 at 120°. C: a, CH_4 at −78°; b, CO at −78°; c, C_3H_8 at 0°; d, *n*-octane at 120°. D: a, CO_2 at 0°; b, C_2H_2 at 0°; c, CH_2Cl_2 at 120°; d, $CHCl_3$ at 120°; e, CCl_4 at 120°.

about 5, 1 and 21 min from CALSG, GELSG and CTLSG columns, respectively (with their highest PL of copper). CALSG columns are superior to those of CTLSG in this respect.

With unsaturated hydrocarbons also, an increase in PL or temperature has the same qualititative effect on t_R. In general, an unsaturated aliphatic hydrocarbon (with one double bond) is eluted after corresponding saturated hydrocarbon from columns of SG and of SMSG. For the same carbon number, the t_R increases with increase in the number of double bonds or when a triple bond replaces a double bond. With increase in temperature and/or PL, these differences in t_R become less prominent. In the region of 6–10% loading of copper, CALSG shows a rise in t_R for the unsaturated compounds (in the temperature range −78° to 30°). This effect did not occur with the other two SMSGs up to the highest loading studied.

CELSG columns were found to be more useful than CALSG columns for the separation of aromatic hydrocarbons also. SG and CTLSG columns do not serve this purpose even at 120°, under the experimental conditions employed, in view of the unusually long t_R exhibited by these compounds. In the region of 6–10% loading

TABLE I

RESULTS OF THERMAL STUDIES

SG = silica gel; CA = Cu ammonium complex; CE = Cu ethylenediamine complex; CT = Cu triethanolamine complex; CALSG, CELSG and CTLSG = SG loaded with CA, CE and CT, respectively. ENT = endothermic peak; EXT = exothermic peak. The conclusions concerning the nature of the decomposition reactions for Nos. 1, 2, 3, 5 and 7 were arrived at from the weight losses observed in TGA carried out in this work. For Nos. 4 and 6, TG data reported in the literature were used.

No.	*Substance*	*Curve in Fig. 2*	*Peak No. and nature*	*Remarks*
1	SG	a	1:ENT	Elimination of H_2O
2	CA*	b	1,2:ENT 3,4:EXT	Stepwise decomposition of the complex to give $CuSO_4$ as the end product[13].
3	CALSG	c	1:ENT 2:EXT	Elimination of H_2O from SG. Partial decomposition of CA.
4	CE**	d	1,2:EXT	Stepwise decomposition of the complex to give CuO as the end product[14].
5	CELSG	e	1:ENT 2:EXT	Elimination of H_2O from SG. Partial decomposition of CE.
6	CT***	—	Two ENT at 215° and 315°	Elimination of the two amine molecules[15].
7	CTLSG	f	1:ENT 2,3:EXT	Elimination of H_2O from SG. Partial decomposition of CT.

* In ref. 13, the final decomposition product was described as CuO.

** Curve and results taken from ref. 14.

*** Results reported in ref. 15 without DTA curve.

of copper, CALSG shows an increase in t_R with increase in PL for the aromatic hydrocarbons also. The fact that this effect occurs even at 120° demonstrates the greater affinity of the aromatic hydrocarbons for CALSG compared with olefins and acetylenes. CELSG does not, however, show this increase in t_R for the aromatic hydrocarbons up to the highest loading studied.

Di-, tri- and tetrachloromethane are not eluted from SG even at 120° or from CTLSG columns up to 60°. They are, however, eluted from CALSG and CELSG columns at 60° (and above) and 30° (and above), respectively. A plot of t_R against chlorine number shows a maximum corresponding to $CHCl_3$ in all instances. While the t_R of CH_2Cl_2 and CCl_4 are closer on CALSG (up to 6% loading), those of $CHCl_3$ and CCl_4 are closer on CELSG and CTLSG. None of the SMSGs has been found to be useful for the separation of all three chloromethanes, owing to the long tailing observed in all instances.

N_2O and CO_2 show very close retention characteristics on SG and all of the SMSGs. This similarity between these two gases has also been found when using many other stationary phases[16–19].

While a monotonic decrease in t_R with increase in PL is the general trend exhibited by most of the gases and vapours studied, C_2H_2, CO_2 and N_2O at 0° and butadiene-1,3 at 30° show a minimum t_R at about a 2% loading of copper (as CA complex), followed by a maximum at about a 4.5% loading (curves a, b and d in Fig. 5B). At this loading (4.5%), even the C_4-alkanes (*n*- and *iso*-) are eluted earlier than C_2H_2. In the 6–10% region, loading seems to have very little effect on the t_R of N_2O and CO_2.

TABLE II

POSSIBLE SEPARATIONS ON SG AND SMSG AT VARIOUS TEMPERATURES

Abbreviations as in Table I. C_1–C_{10} represent the *n*-alkanes.

Temperature (°C)	*Mixture separated*	*Column*	*PL of copper*	*Remarks*
−78	He, O_2–N_2–Ar, CO, CH_4	SG	—	At 0° and above, these gases elute together. The SMSG columns do not separate this mixture even at −78°
	C_1, C_2 and C_3	CELSG	3–4	C_4 and higher show very long t_R
0	Air–He–CO–C_1, C_2, CO_2–N_2O and C_2H_2–C_3	SG	—	
	C_1–C_4	CALSG	2.3	
		CTLSG	1–4	
	C_3, C_4, butene-1 and butadiene-1,3	CALSG	6–10	C_2H_2 elutes with C_4.
		CELSG	2–2.5	C_2H_2 elutes with C_3.
	C_4–butene-1–butadiene-1,3, C_5 and C_6	CELSG	3–4	
30	C_1, C_2, CO_2–N_2O, C_3–C_2H_2, C_4, butene-1 and butadiene-1,3	SG	—	Even at 60°, C_5 takes a very long time to elute
	C_2–C_5–butene-1, butadiene-1,3 and C_6	CELSG	0.9	
	C_5–C_8	CELSG	3–4	
	CH_2Cl_2, CCL_4–$CHCl_3$	CELSG	1–4	
60	C_2–C_5, butene-1, butadiene-1,3 and C_6	CALSG	2.3–4.5	
	C_4, C_5, butene-1, C_6–butadiene-1,3 C_7 and C_8	CALSG	6–10	
	C_5, C_6, C_7–C_6H_6, C_8–C_7H_8, C_8H_{10} and C_9	CELSG	3.8	
	C_2, C_3, C_4, butene-1, butadiene-1,3–C_5	CTLSG	1–4	
	CH_2Cl_2–CCl_4 and $CHCl_3$	CALSG	2.3–4.5	
	CH_2Cl_2 and $CHCl_3$–CCl_4	CALSG	6–10	
		CELSG	1–2	
120	C_2, CO_2–N_2O–C_3–C_2H_2, C_4, butene-1, butadiene-1,3 and C_5	SG	—	
	C_4, C_5, C_6, C_7–C_6H_6, C_8, C_7H_8, C_8H_{10}	CALSG	6–10	
	C_5, C_6, C_7, C_6H_6, C_8, C_7H_8, C_9 and C_8H_{10}	CELSG	2–2.6	
	C_7–C_6H_6, C_8–C_7H_8, C_9–C_8H_{10}, C_{10}	CELSG	3.3	
	C_3, C_4, butene-1, butadiene-1,3–C_5, C_6, C_7 and C_8	CTLSG	2–3.3	
	CH_2Cl_2–CCl_4 and $CHCl_3$	CALSG	2.3	
		CELSG	0.9	
	CH_2Cl_2 and CCl_4–$CHCl_3$	CTLSG	1–4	

However, C_2H_2 and other unsaturated hydrocarbons show an increase in t_R in this region. At 60°, the peaks in the t_R *versus* PL curves become less prominent and at 120° they disappear. All of these results clearly exclude the possibility of surface area playing a significant role in these instances. Polarity, chemical affinity, the degree and nature of unsaturation, etc., seem to play their own significant role in deciding the interactions between these gases and CALSG and shaping the t_R *versus* PL profiles.

The above gases, on the other hand, show a continuous decrease in t_R with increase in PL when CE or CT is loaded on SG (curves a, b and d in Fig. 6A; curves a and b in Fig. 6D). The differences in the nature of the t_R *versus* PL profiles in the three instances suggests a corresponding difference in the nature of the forces responsible for shaping the retention behaviour.

The elution of oxygenated organic compounds takes inconveniently long times on SG and all of the SMSGs which therefore do not seem to have any practical utility in separating such compounds.

The nature of some of the possible GC separations is illustrated by the chromatograms in Figs. 7 and 8.

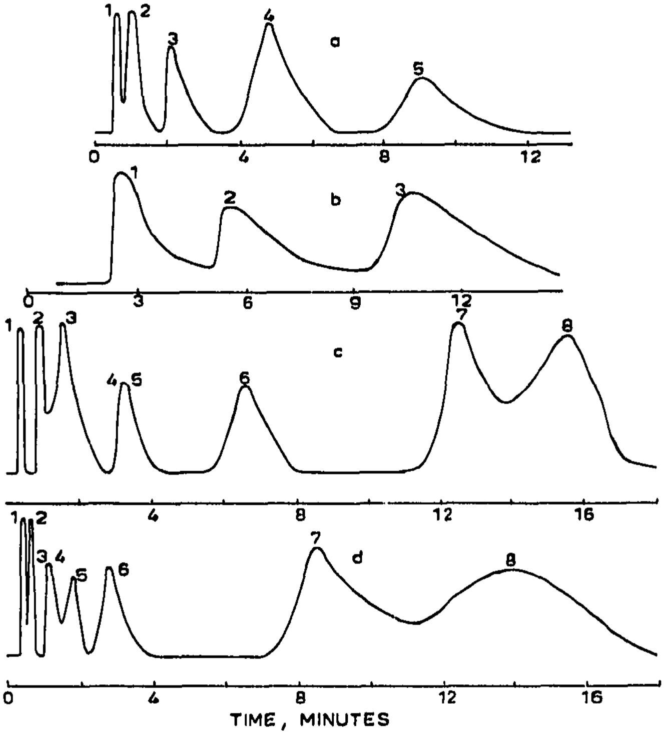

Fig. 7. GC separations on SG and CALSG. a: Loading, 10% as copper; temperature, 120°; (1)–(5) = C_5–C_9 *n*-alkanes. b: Loading, 6% as copper; temperature, 120°; (1) benzene; (2) toluene; (3) xylene. c: SG at 30°; (1) CH_4; (2) C_2H_6; (3) CO_2–N_2O; (4) C_3H_8; (5) C_2H_2; (6) *n*-C_4H_{10}; (7) butene-1; (8) butadiene-1,3. d: CALSG at 30° with 2.35% copper; (1)–(8), as in c.

ACKNOWLEDGEMENTS

Shri A. G. Datar is grateful to the Department of Atomic Energy for a Junior Research Fellowship under the Bombay University–B.A.R.C. Collaboration Pro-

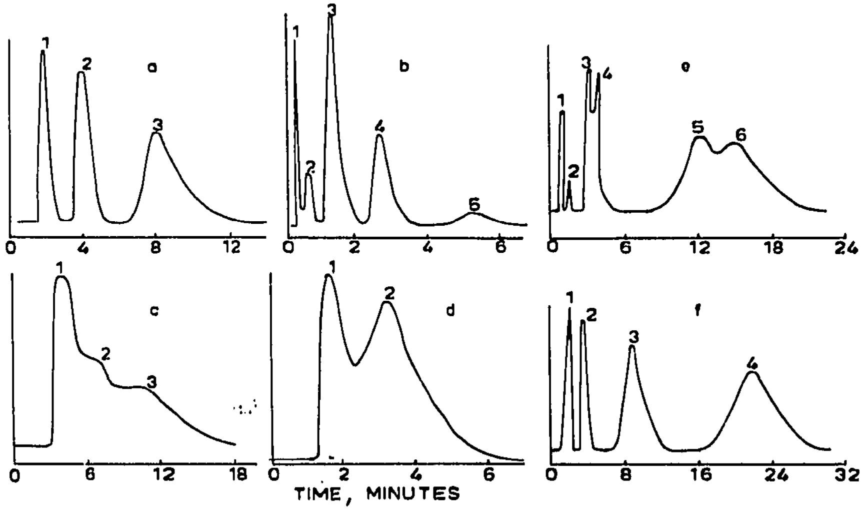

Fig. 8. GC separations on CELSG and CTLSG. a to d, CELSG; e and f, CTLSG. a: Temperature, 120°; loading, 2.6% as copper; (1) benzene; (2) toluene; (3) xylene. b: temperature, 120°; loading, 3.5% as copper; (1)–(5), C_6–C_{10} *n*-alkanes. c: temperature, 60°; loading, 0.88% as copper; (1) CH_2Cl_2; (2) $CHCl_3$; (3) CCl_4. d: temperature, 30°; loading, 3.3% as copper; (1) CH_2Cl_2; (2) $CHCl_3$–CCl_4. e: temperature, 0°; loading, 1.1% as copper; (1) CH_4; (2) C_2H_6; (3) C_3H_8; (4) C_2H_2; (5) isobutane; (6) *n*-butane. f: temperature, 120°; loading, 4.0% as copper; (1)–(4), C_5–C_8 *n*-alkanes.

gramme. The authors thank Dr. M. Sankar Das, Head, Analytical Chemistry Division, and Dr. Ch. Venkateswarlu for very helpful suggestions during the preparation of the manuscript.

REFERENCES

1 J. P. Okamura and D. T. Sawyer, *Separ. Purif. Methods*, 1 (1972) 409; and references cited therein.
2 C. Vidal Madjar and G. Guichon, *Separ. Purif. Methods*, 2 (1973) 1; and references cited therein.
3 C. G. Scott, in M. van Swaay (Editor), *Gas Chromatography*, Butterworths, London, 1962, p. 36.
4 N. Dimov, *Abh. Deut. Acad. Wiss. Berlin, Kl. Chem. Geol. Biol.*, 2 (1966) 133.
5 D. A. Vyakhirev, A. Ya. Bruk and N. M. Olefirenko, *Abh. Deut. Acad. Wiss. Berlin, Kl. Chem. Geol. Biol.*, 2 (1966) 137.
6 J. N. Gerber and D. T. Sawyer, *Anal. Chem.*, 44 (1972) 1199.
7 C. S. G. Phillips and C. G. Scott, in J. H. Purnell (Editor), *Progress in Gas Chromatography*, Interscience, New York, 1967, p. 121.
8 N. C. Saha and S. K. Ghosh, *Technology* (Coimbatore, India), 5 (1968) 220.
9 K. S. Subramanian, *B.A.R.C. Report*, No. 429, 1969.
10 F. M. Nelson and F. T. Eggertsen, *Anal. Chem.*, 30 (1958) 1387.
11 R. K. Bhat and T. S. Krishnamoorthy, *Indian J. Technol.*, in press.
12 P. S. Ramanathan, O. P. Srivastava and Ch. Venkateswarlu, *B.A.R.C. Report*, No. 574, 1971.
13 W. W. Wendlendt and T. M. Southern, *Anal. Chim. Acta*, 32 (1965) 405.
14 W. W. Wendlendt, *J. Inorg. Nucl. Chem.*, 25 (1963) 833.
15 G. N. Rao and S. C. Rustagi, *Indian J. Chem.*, 2 (1971) 1390.
16 V. S. Sarang, P. S. Ramanathan and Ch. Venkateswarlu, *Indian J. Technol.*, 12 (1974) 37.
17 A. G. Datar, P. S. Ramanathan and M. Sankar Das, *Indian J. Technol.*, 12 (1974) 127.
18 A. G. Datar, P. S. Ramanathan and M. Sankar Das, *J. Chromatogr.*, 93 (1974) 217.
19 V. S. Sarang, P. S. Ramanathan and Ch. Venkateswarlu, unpublished work.